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HALL EFFECT INVESTIGATIONS QUARTERLY PROGRESS REPORT

1 JANUARY TO 31 MARCH 1963

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ABSTRACT

The properties of Cu-doped p-type films of InSb on pyrex substrates are described in terms of the two-band charge carrier model applied to bulk crystalline InSb. The calculated virtual mobility ratio is shown to be of the order of 32, which is in fair agreement with values expected from the polycrystalline material. Data from present and past experiments on annealing and recrystallization of vacuum-deposited films are in agreement.

FOREWORD

A continuing study of the Hall effect in thin semiconductor films is being conducted at the Naval Ordnance Laboratory, as authorized by the Bureau of Naval Weapons WepTask RREN-04-371/211-1/F008-01-15. This work is aimed toward the development of thin film Hall generators and other devices based upon the Hall effect. Electrical and electronic components and circuits employing this phenomenon are also being investigated.

This third quarterly report covers the period 1 January to 31 March 1963.

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INTRODUCTION

Previous progress reports (Refs. 1 and 2) discussed the properties of indium antimonide films produced by means of the three-temperature control process. It was shown that considerable scatter in the electron mobility μ and the conductivity σ were found in films produced sequentially under conditions of evaporation and processing assumed to be identical.

All the films were n-type throughout a temperature range of 373 to 87°K. The scatter in μ and σ could be due to a variety of causes; two of these were selected for further investigations.

1. The size of the crystallites making up the film has a considerable effect on the virtual electron mobility. Consequently, the development of methods for growing films composed of a few large crystals is desirable. One such method was discussed in the last progress report (Ref. 2). Further studies along this line were carried out during this reporting period and will be continued.
2. The compensation by acceptor impurities, of either impurity-activated or intrinsically generated electrons was considered to be another possible reason for the observed scatter. This is particularly likely if the impurities diffuse rapidly through the film during its formation and if the concentration of such impurities varies during sequential evaporations.

It has been found that copper acts as a p-type impurity in InSb and, even in very small concentration, tends to create a compensation effect such as proposed above. Since Cu is present in the evaporation chamber (Ref. 3) as part of the cooling system and other fixtures, its effects need to be considered in the evaluation of the galvanomagnetic properties of films produced by present techniques.

In this report, the properties of InSb films, deliberately Cu-doped, will be discussed in terms of the two-band model applied to bulk InSb. Data will also be presented on further annealing and alloying studies of InSb films deposited on pyrex substrates.

GENERAL RELATIONS FOR THE MIXED CONDUCTIVITY REGION OF InSb FILMS

In the discussion below, the following assumptions are made:

1. The InSb film is a semiconductor obeying classical statistics, the electrons and holes being contributed by intrinsic generation as well as by impurity activation.
2. The temperature region is that in which all donors and acceptors are and remain ionized.
3. Surfaces of constant energy in momentum space are spherical.
4. Mean free paths of both holes and electrons are independent of energy. This is true if thermal scattering is the only significant scattering mechanism; i.e., if scattering from ionized impurity centers is disregarded.

The relations for the Hall coefficient R_h and the conductivity σ (Ref. 1) are then

$$R_h = \left(-\frac{1}{e} \right) \frac{nb^2 - p}{(nb + p)^2} \sigma = ne\mu_n + pe\mu_p \quad (1)$$

where

- n = the electron concentration per cm^3
- p = the hole concentration per cm^3
- $b = \mu_n/\mu_p$, the ratio of the electron to hole mobilities
- e = charge on the electron

In this equation it is considered that the drift mobility μ_d and the Hall mobility μ_H are equal.

Let the concentration per cm^3 of donors be N_D and that of acceptors be N_A . Then

$$p - N_A = n - N_D \quad (2)$$

Solving equation (2) for p and substituting this value in equation (1) yields

$$R_h = \left(-\frac{1}{e} \right) \frac{n(b^2 - 1) - N_A + N_D}{[n(b + 1) + N_A - N_D]^2} \quad (3)$$

The maximum value of R_h may be determined from $dR_h/dn = 0$; hence, from equation (3)

$$\frac{dR_h}{dn} = \frac{b^2 - 1}{[]^2} - 2(b+1) \frac{n(b^2 - 1) - N_A + N_D}{[]^3} = 0 \quad (4)$$

which becomes

$$(b^2 - 1)[n(b+1) + N_A - N_D] = 2(b+1)[n(b^2 - 1) - N_A + N_D] \quad (5)$$

Dividing by $(b^2 - 1)$ yields

$$n(b+1) + N_A - N_D = 2(b+1) \left(n - \frac{N_A - N_D}{b^2 - 1} \right) \quad (6)$$

Solving for n gives

$$N_A - N_D + 2(b+1) \left(\frac{N_A - N_D}{b^2 - 1} \right) = 2n(b+1) - n(b+1) \quad (7)$$

Hence

$$(N_A - N_D)(b^2 - 1) + 2(b+1)(N_A - N_D) = n(b+1)(b^2 - 1) \quad (8)$$

By collecting terms

$$(b+1)[(b-1)(N_A - N_D) + 2(N_A - N_D)] = n(b+1)(b^2 - 1) \quad (9)$$

Hence

$$(N_A - N_D)(b+1) = n(b^2 - 1) \quad (10)$$

Therefore, at the temperature at which R_h is a maximum,

$$n_m = \frac{b+1}{b^2 - 1} (N_A - N_D) = \frac{N_A - N_D}{b - 1} \quad (11)$$

The value of n from equation (11) is substituted in equation (3) to yield the value of R_{hm} .

$$R_{hm} = \left(-\frac{1}{e}\right) \frac{\left(\frac{N_A - N_D}{b-1}\right)(b^2 - 1) - (N_A - N_D)}{\left[\left(\frac{N_A - N_D}{b-1}\right)(b+1) + (N_A - N_D)\right]^2} \quad (12)$$

By rearranging terms and performing the required algebraic manipulations, this becomes

$$R_{hm} = -\left[\frac{(b-1)^2}{e}\right] \left\{ \frac{(N_A - N_D)(b-1)b}{[2b(N_A - N_D)]^2} \right\} \quad (13)$$

Thus

$$R_{hm} = \left(-\frac{1}{4be}\right) \left[\frac{(b-1)^2}{N_A - N_D} \right] \quad (14)$$

Now consider the situation in the extrinsic (impurity-activated) temperature region. Let the electron concentration n be zero; then from equation (2) $p = N_A - N_D$, and from equation (3)

$$R_{hx} = \left(\frac{1}{e}\right) \left(\frac{1}{N_A - N_D}\right) \quad (15)$$

The ratio of R_{hm}/R_{hx} is therefore, by means of equations (14) and (15),

$$\frac{R_{hm}}{R_{hx}} = -\frac{(b-1)^2}{4b} \quad (16)$$

A minimum in R_h may be determined from equation (1)—i.e., $nb^2 = p$, and from equation (3)—i.e., $n(b^2 - 1) = N_A - N_D$. Both of these correspond to $R_h = 0$. Note that if $(R_h)_{ex}$ is determined experimentally the quantity $(N_A - N_D)$ may be calculated. Since, in general,

$$np = n_i^2 \quad (17)$$

introducing equation (2) into equation (17) yields

$$n(n + N_A - N_D) = n_i^2 \quad (18)$$

Consequently, $n^2 + n(N_A - N_D) = n_i^2$; thus

$$n = -\frac{(N_A - N_D)}{2} \pm \frac{1}{2} \left[(N_A - N_D)^2 + 4n_i^2 \right]^{\frac{1}{2}} \quad (19)$$

Therefore, if n_i is known at any temperature, n may be calculated, provided that $(N_A - N_D)$ has first been determined in the extrinsic region. Equation (11) may now be rewritten

$$n_m = \frac{N_A - N_D}{b - 1} = -\frac{N_A - N_D}{2} \pm \frac{1}{2} \left[(N_A - N_D)^2 + 4n_i^2 \right]^{\frac{1}{2}} \quad (20)$$

Solving for this yields

$$(N_A - N_D) \left(\frac{1}{b - 1} + \frac{1}{2} \right) = \frac{1}{2} \left[(N_A - N_D)^2 + 4n_i^2 \right]^{\frac{1}{2}} \quad (21)$$

which, upon further algebraic manipulation, becomes

$$(N_A - N_D) \left(\frac{b + 1}{b - 1} \right) = \left[(N_A - N_D)^2 + 4n_i^2 \right]^{\frac{1}{2}} \quad (22)$$

$$(N_A - N_D)^2 \left(\frac{b + 1}{b - 1} \right)^2 = (N_A - N_D)^2 + 4n_i^2 \quad (23)$$

By collecting terms, this becomes

$$(N_A - N_D)^2 \left[\frac{(b + 1)^2}{(b - 1)^2} - 1 \right]^2 = 4n_i^2 = (N_A - N_D)^2 \left[\frac{(b + 1)^2 - (b - 1)^2}{(b - 1)^2} \right] \quad (24)$$

Consequently,

$$4n_i^2 = (N_A - N_D)^2 \left[\frac{b^2 + 2b + 1 - b^2 + 2b - 1}{(b - 1)^2} \right] \quad (25)$$

Therefore, at the temperature for which R_h is a maximum,

$$n_{im} = (N_A - N_D) \left(\frac{b^{\frac{1}{2}}}{b - 1} \right) \quad (26)$$

Equation (26) may, however, be derived in a much simpler fashion. In equation (18), note that

$$n_{im}^2 = n_m^2 + n_m (N_A - N_D) \quad (27)$$

Replacing n_m in equation (27) by its value in equation (18)

$$n_i^2 = \left(\frac{N_A - N_D}{b - 1} \right)^2 + \left(\frac{N_A - N_D}{b - 1} \right)^2 = (N_A - N_D)^2 \frac{b}{(b - 1)^2} \quad (28)$$

which immediately yields equation (27).

EXPERIMENTAL

Figure 1 shows the Hall voltage v_h as a function of drive current i_h in a constant magnetic field of $H = 5 \times 10^3$ oersteds at 23°C ambient, for a Cu-doped InSb film on glass (Sample 88A). The Hall voltage is linear in i_h for values smaller than 10 ma. For higher drive currents v_h rises in a nonlinear manner because of induced Joule heating in the sample. The Hall coefficient therefore rises with temperature, contrary to the behavior of the undoped InSb films, which exhibit a decrease in R_h with temperature (Ref. 1).

Figure 2 shows R_h as a function of the reciprocal absolute temperature for the sample measured in the linear region defined by v_h as a function of i_h . The curve is typical of p-type InSb, showing a maximum in R_h and an inversion in sign below the temperature at which $R_h = 0$. Data for R_h was obtained in the linear region of a curve like that of Figure 1. Subsequent tests for the thermoelectric potential between a hot and cold junction in contact with the sample while the latter was immersed in liquid nitrogen showed that, in the extrinsic region, the charge carriers are holes.

Figure 3 shows the dependence of the sample conductivity σ upon the absolute temperature. The conductivity was determined from two-terminal measurements of resistance made across the drive electrodes and the geometry of the sample. The thickness was determined from

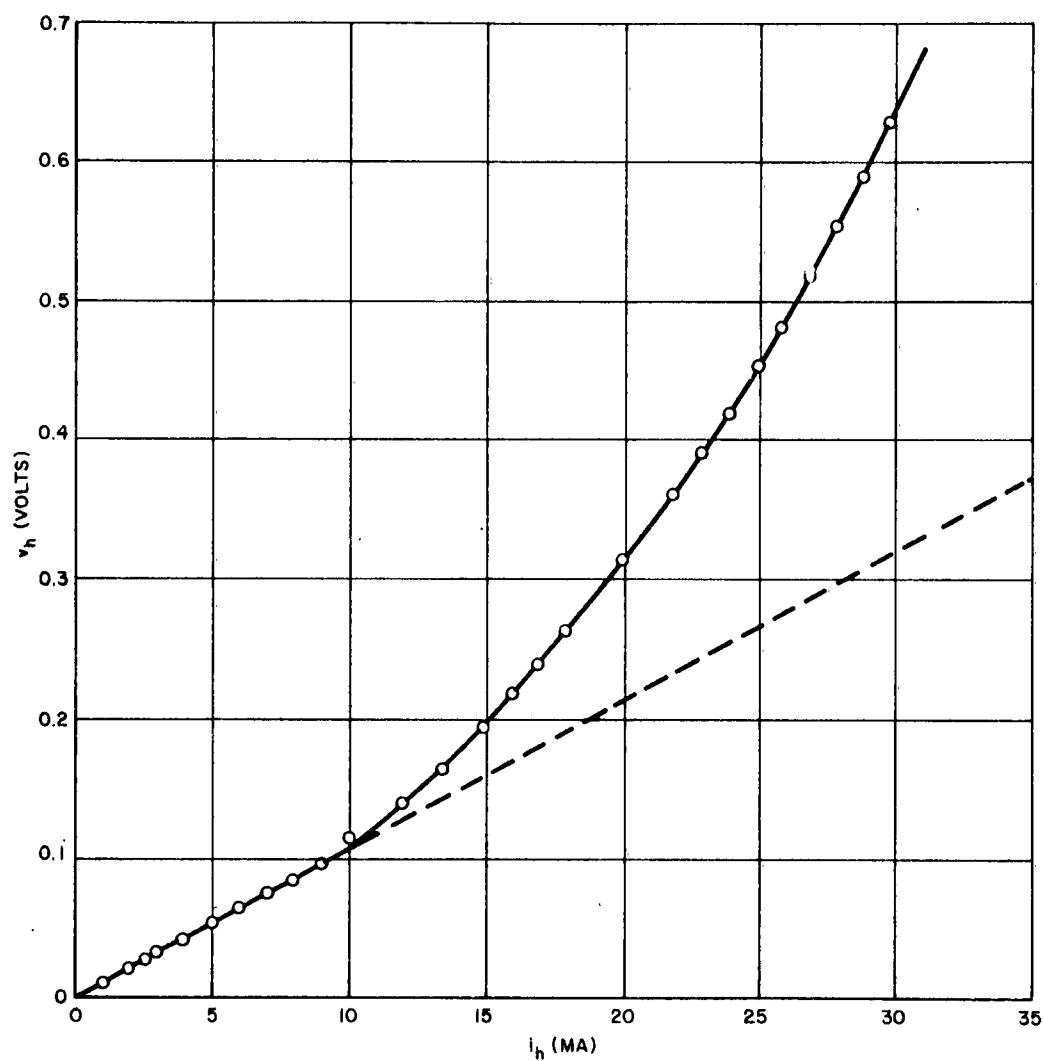


FIGURE 1. Hall Voltage Dependence Upon Drive Current of a Cu-Doped InSb Film at 23°C in a Magnetic Field of 5×10^3 Oersteds

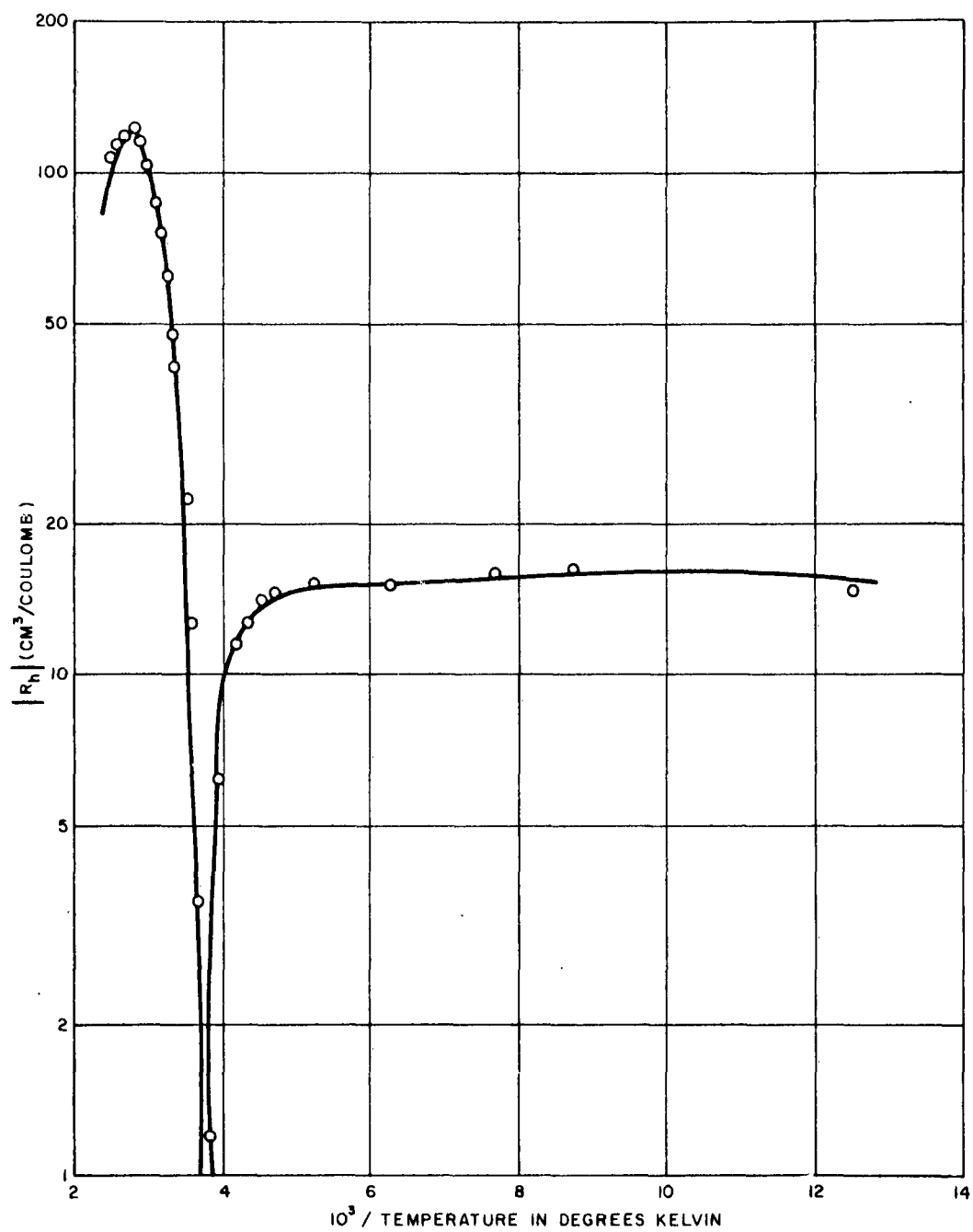


FIGURE 2. Dependence of the Hall Coefficient Upon the Absolute Reciprocal Temperature for a Cu-Doped InSb Film in a Magnetic Field of 5×10^3 Oersteds

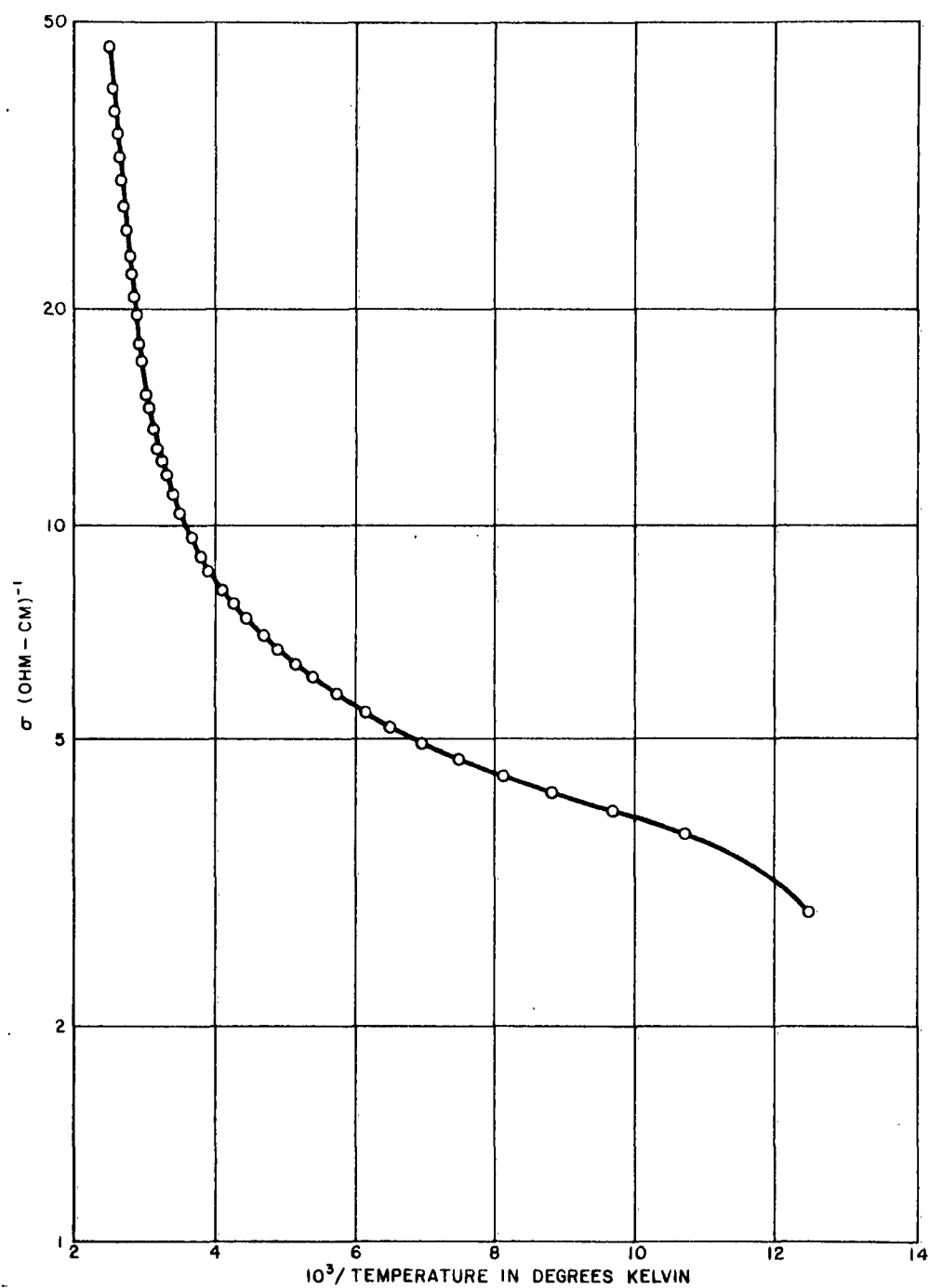


FIGURE 3. Dependence of the Electrical Conductivity Upon the Reciprocal Absolute Temperature at Zero Magnetic Field for a Cu-Doped InSb Film

infrared reflection interference measurements (Ref. 3) and is at best an average value. The dispersion across the sample is not known. Therefore, the conductivity values shown in Figure 3 should be regarded as nominal although, over the temperature region shown, the values are self-consistent to within the experimental error estimated at less than 2 percent. By taking the drift mobility μ_d to be identical with the Hall mobility μ_H , the concentration of impurities may be determined from the temperature-independent extrinsic Hall coefficient R_h in Figure 2.

Since $(R_h)_m = -120 \text{ cm}^3/\text{coul}$ and $(R_h)_x = 16 \text{ cm}^3/\text{coul}$, then from equation (16)

$$-\frac{(R_h)_m}{(R_h)_x} = -7.5 = -\frac{(b-1)^2}{4b}$$

and therefore

$$30b = (1-b)^2 \quad (29)$$

The mobility ratio b is therefore

$$b = 16 \pm \frac{1}{2}(32^2 - 4)^{\frac{1}{2}} = 16 \pm \frac{1}{2}(1020)^{\frac{1}{2}} = 16 \pm 15.97 \quad (30)$$

By rejecting the negative root it is found that

$$b = 32 \quad (31)$$

The impurity concentration may now be calculated from equation (15) as

$$\begin{aligned} (N_A - N_D)^{-1} &= e(R_h)_x = (1.6)(10^{-19}) 16 = (2.56)(10^{18}) \\ (N_A - N_D) &= (3.91)(10^{17}) \text{ holes/cm}^3 \end{aligned} \quad (32)$$

By using equation (11), the electron concentration at the temperature for which R_h is a maximum is

$$n_m = \frac{(3.91)(10^{17})}{31} = (1.26)(10^{16}) \text{ electrons/cm}^3 \quad (33)$$

By means of equation (2), hole concentration at the same temperature is

$$p_m = (3.91)(10^{17}) + (0.126)(10^{17}) = (4.04)(10^{17}) \text{ holes/cm}^3 \quad (34)$$

By using equation (26), the intrinsic electron concentration at the same temperature is

$$(n_i)_{mx} = (3.91)(10^{17}) \frac{5.65}{31} = (7.12)(10^{16}) \text{ electrons/cm}^3 \quad (35)$$

It is seen, therefore, that the hole concentration is nearly one order of magnitude larger than the intrinsic electron concentration at $R_h = R_{hm}$ and thus causes a considerable compensation effect. The general expression for the conductivity is $\sigma = e\mu_p [n(b+1) + N_A - N_D]$ and since $\sigma_m = 23.5 \text{ (ohm-cm)}^{-1}$ from Figure 3, it follows that

$$\mu_{pm} = \frac{\sigma_m}{e[n_m(b+1) + N_A - N_D]} \quad (36)$$

The hole mobility for $R_h = R_{hm}$ is therefore given by

$$\mu_{pm} = \frac{23.5}{(1.6)(10^{-19})(1.26)(10^{16})(33 + 39.1)(10^{16})} \quad (37)$$

Thus, the hole mobility is

$$\mu_{pm} = 182 \text{ cm}^2 \text{ (volt-sec)}^{-1} \quad (38)$$

and the electron mobility μ_n is

$$\mu_n = 32\mu_p = 5.824 [10^3 \text{ cm}^2 \text{ (volt-sec)}^{-1}] \quad (39)$$

These mobilities are considerably lower than the values to be expected from bulk InSb. However, even in n-type films of InSb the electron mobilities are smaller by a factor of three than in the crystalline material. The origin of the scattering mechanism responsible for this effect is not yet known.

The electron and hole concentrations may be calculated quite easily at the temperature where $R_h = 0$ since $n_0 b^2 = p_0$. Equation (2) still applies and it follows that

$$n_0 + N_A - N_D = m_0 b^2 \quad (40)$$

If the mobility ratio is assumed to be essentially temperature-independent over the temperature range between R_{hm} and $R_h = 0$, then

$$\begin{aligned} n_0 &= (3.82)(10^{14}) \text{electrons/cm}^3 \\ p_0 &= (3.91)(10^{17}) \text{holes/cm}^3 \end{aligned} \quad (41)$$

The conductivity at this temperature may be expressed in terms of equation (1) as

$$\sigma = en_0 \mu_{n0} (1 + b) \quad (42)$$

Using the value $\sigma_0 = 9 (\text{ohm-cm})^{-1}$ determined from Figure 3 and the n_0 calculated above, the electron mobility decreased from its value at $R_h = R_{hm}$ to $\mu_{n0} = 4460 \text{ cm}^2/(\text{volt-sec})$ at $R_h = 0$. The hole mobility is then

$$\mu_{p0} = \frac{\sigma_0/e}{n_0(b+1) + N_A - N_D} \quad (43)$$

Hence, $\mu_{p0} = 139 \text{ cm}^2/(\text{volt-sec})$. Since it has been assumed that b is a constant, both μ_n and μ_p have decreased from their value at R_{hm} to $R_h = 0$ by approximately 24 percent.

The concentration of intrinsically generated electrons at the temperature for which $R_h = 0$ may be derived by means of equation (18) is

$$n_{i0}^2 = n_i^2 + n_i(N_A - N_D) \quad (44)$$

With equation (40) substituted into (44)

$$n_{i0} = (N_A - N_D) \left(\frac{b}{b^2 - 1} \right) \quad (45)$$

The intrinsic electron concentration at this temperature is therefore $n_{i0} = (1.22)(10^{16}) \text{electrons/cm}^3$, which may be contrasted with the earlier calculated value of $n_{im} = (7.12)(10^{16}) \text{electrons/cm}^3$ at $R_h = R_{hm}$.

The concentration of intrinsically generated electrons in InSb may be expressed to a fair approximation (Ref. 4) as

$$n_i \approx (5.7)(10^{14} T^{3/2}) \exp(-0.125/kT) \quad (46)$$

Thus, using equation (45) with $A = (5.7)(10^{14} T^{3/2})$,

$$\frac{b(N_A - N_D)}{A(b^2 - 1)} = \exp(-0.125/kT) \approx \frac{N_A - N_D}{Ab} \quad (47)$$

Consequently, since $k = (8.63)(10^{-5} \text{ ev} \cdot \text{K}^{-1})$,

$$\frac{(1.448)(10^3)}{T_0} = \log Ab - \log (N_A - N_D) \quad (48)$$

Thus, the temperature T_0 at which $R_h = 0$ is given as a function of the impurity concentration is

$$T_0 = \frac{(1.448)(10^3)}{\log Ab - \log (N_A - N_D)} \quad (49)$$

An increase in the concentration of acceptor centers leads to an upward shift in T_0 . An increase in the Cu concentration should, therefore, lead to a displacement of T_0 toward higher temperatures; this was verified experimentally. Since $b \gg 1$ in InSb, the ratio (n_{im}/n_{i0}) may be expressed as

$$\frac{n_{im}}{n_{i0}} = \frac{(b+1)}{b^{\frac{1}{2}}} \approx b^{\frac{1}{2}} \quad (50)$$

With $b^{\frac{1}{2}} = 5.65$, $n_{im} = (7.12)(10^{16})$ electrons/cm². It follows that n_{i0} should be $(1.26)(10^{16})$ electrons/cm³. This, of course, is in fair agreement with the value of $n_{i0} = (1.22)(10^{16})$ electrons/cm³ calculated by means of equation (45).

The experimental data presented here illustrate the significant effect of Cu in doping InSb films. Since, for the present, we are concerned primarily with obtaining uncompensated electronic conduction in these films, efforts will be made to keep acceptor impurities out of the evaporation system in the hope of obtaining better reproducibility of deposition.

The properties and application of other p-type doped films are reserved for further extensive investigations.

RECRYSTALLIZED InSb FILMS ON PYREX

The procedure for recrystallizing InSb films described in the last progress report (Ref. 2) was used on additional films in order to confirm the advantages of this post-evaporation processing. A summary of the experimental data is shown in Table 1. The resistance of the films has decreased by a factor of 10 to 30; the mobility has increased by a factor of 5 to 10.

The improvement in the films as a result of the recrystallization may be seen in:

1. A decrease in the effective resistance of individual Hall generators and consequently a smaller voltage drop across them for a given Hall current. Since the maximum Hall current is limited by the thermal dissipation of the film and substrate, higher currents may be applied to the samples after recrystallization processing without exceeding the nominal value imposed by the onset of Joule heating.
2. For a fixed magnetic field sensitivity expressed as (v_h/B) , the recrystallized films exhibit a smaller input power dissipation and consequently a smaller thermal drift of the misalignment potential.

Assuming that the magnetic field sensitivity (v_h/B) is a parameter held constant before and after recrystallization, the ratio of P_b , the input power before annealing, to P_a , the power required after annealing in order to obtain this sensitivity, is

$$(P_b/P_a) = \frac{(v_h/iB)^2 \text{ after } \left(\frac{r_b}{r_a}\right)}{(v_h/iB)^2 \text{ before}}$$

In a similar fashion the input potential to the Hall plate before and after annealing and recrystallization is given by

$$(v_b/v_a) = \frac{(v_h/iBr_0) \text{ after}}{(v_h/iBr_0) \text{ before}}$$

In view of the results illustrated in the following table and the earlier data (Ref. 2), the advantages of the recrystallization process are considered to be firmly established. It is apparent that the process

TABLE 1. DATA ON InSb FILMS ON PYREX, BEFORE AND AFTER BEING INDIUM-COATED AND RECRYSTALLIZED

Sample	v_H/iBr_0 (All values $\times 10^{-6}$)		r_0		v_H/iB		Input Voltage (v_b/v_a)	Input Power (P_b/P_a)
	Before	After	Before	After	Before	After		
103A	4.1	35.4	3010	115	0.0123	0.0041	8.6	2.9
103B	4.1	32.0	3010	276	0.0123	0.0088	7.8	5.6
103C	4.1	32.8	3010	108	0.0123	0.0035	8.0	2.25
104A	4.6	11.9 (partially boiled off)	835	730	0.0038	0.0087	2.6	6.0
104B	4.6	22.0	835	81	0.0038	0.0018	4.8	2.3
105A	4.4	23.7	1650	81	0.0073	0.0019	5.4	1.4
105B	4.4	24.9	1650	58	0.0073	0.0014	5.6	1.05
105C	4.4	21.7	1650	60	0.0073	0.0013	4.9	0.87
106A	2.7	30.9	1630	33	0.0044	0.0010	11.4	2.55

should apply to other semiconductors as well. Additional procedures for improving the crystallinity of the deposit will be investigated during the next reporting period.

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